SOLID FUNGICIDE

Detailed Description of the Invention

The present invention relates to a solid fungicide which acts directly on fungi which develop on and attach to the surfaces of interior and exterior building materials, and kills them, while also providing a newly cleaned surface by bleaching the action surface. The fungicide of the invention may be used with particular advantages in the form of a stick fungicide housed in a container.

Prior Art

Removal of fungi which develop on and attach to the surfaces of interior and exterior building materials has conventionally been accomplished with a wide variety of different types of fungicides. Because fungi tend to develop in large amounts particularly on the constantly moist parts, such as the walls (particularly the joints between tiles), of bathrooms, kitchens and wash basins, a number of fungicides are normally provided in the form of combinations of strong alkalis such as sodium hydroxide with strong oxidizing agents such as hypochlorous acid salts, and this form is usually a liquid stored in container, which can be absorbed by a cloth or sponge and applied to the sections from which fungi are to be eliminated, or if the container is a spray container, a suitable amount of the liquid is sprayed for application onto those sections.

Incidentally, when an appropriate amount of the liquid is used by absorption into a separate material as in the former case, the process is laborious since the amount must be measured each time, and troublesome gloves must be worn to protect the hand during handling of the liquid. Also, when the liquid is sprayed from a spray container as in the latter case, it has been impossible to avoid needless spraying of the liquid not only on the target section from which fungi are to be eliminated, but also onto the surrounding sections which require no spraying. Consequently, the liquid spraying method is not only economically wasteful, but when used in small bathrooms, kitchens and wash basins the concentration of sprayed fungicide particles floating in the air increases, producing characteristic irritating odors which create discomfort for the user and sometimes even result in

accidents due to inhalation of the sprayed particles by the user, or the scattered sprayed particles may adhere to the skin, often causing skin rash.

Wipeable type fungicides provided with felt applicators have been proposed as a means of solving the problems described above. Because such fungicides can be used with the liquid fungicide included in the applicator, it is possible to avoid the inconvenience referred to above, and they are therefore noteworthy especially since they prevent or reduce the occurrence of accidents caused by sprayed particles. Nevertheless, when the fungicide is included in an applicator, it is difficult to prevent dripping of excess liquid (liquid drip) from the applicator. Liquid drip indicates that an excess amount of the fungicide is being used, which can be economically undesirable, and it can easily be seen that as long as fungicides are in such liquid forms there will exist the danger of generation of chlorine gas by their use in admixture with acidic cleaning agents.

Fungicides composed mainly of oxygen-based bleaching agents, particularly hydrogen peroxide, reduce the danger of chloride gas generation by use of admixture with acidic cleaning agents. Such types of fungicides are often inadequately effective for killing large amounts of fungi because hydrogen peroxide is an alkali and unstable, rendering the fungicides themselves weakly acidic. That is, when using fungicides composed mainly of oxygen-based bleaching agents, the operation for elimination of the fungi must be carried out more frequently. Furthermore, although lactic acid-based fungicides are known which contain no bleaching components, such fungicides upon killing the fungi leave the color of the fungi as a smudge, and therefore hardly result in an adequate cleaning effect.

Problems to be Solved by the Invention

It is an object of the present invention to overcome the aforementioned problems of the prior art by providing an improved fungicide which acts directly on fungi and kills them, while also providing a newly cleaned surface by bleaching the action surface, and which can exhibit a reliable fungicidal effect and cleaning effect through safe and easy use, without waste.

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Means for Solving the Problems

According to the present invention, the above-mentioned object can be achieved by a solid fungicide characterized by containing an oxidation-type bleaching agent as an effective component and comprising a gelling agent for solidification of the bleaching agent.

Preferred Embodiments of the Invention

Preferred embodiments of the present invention will now be described.

The present inventors, upon reflecting on the fact that the aforementioned problems of the prior art are a result of the use of fungicides in liquid form, considered that many heretofore unimagined advantages might be afforded if they could be used in solid form, and thus upon testing solidification of various effective components we have arrived at the present invention.

That is, the solid fungicide of the invention is characterized by employing an oxidation-type bleaching agent as the effective component and a gelling agent for solidification of the bleaching agent.

For carrying out the invention, the oxidation-type bleaching agent used as the effective component may be any one or combination of two or more compounds appropriately selected from among those known in the field of fungicides to have excellent fungicidal and bleaching properties. The oxidation-type bleaching agent in the fungicide of the invention exhibits an excellent oxidizing effect, thus killing fungi while also bleaching (pigment bleaching) sections which have been blackened or otherwise colored by the fungi.

Examples of oxidation-type bleaching agents which can be advantageously used include alkali metal salts and alkali earth metal salts, for example sodium salts, potassium salts and calcium salts, of halogen oxyacids, for example hypohalogenous acids such as hypochlorous acid and hypobromous acid, halogenous acids such as chlorous acid and bromous acid, and halogenic acids such as chloric acid and bromic acid, with preferred examples being sodium hypochlorite, potassium hypochlorite and calcium hypochlorite. Also, other chlorine sources such as sodium chloride, calcium chloride, potassium chloride and other chlorides may also be added.

Of the bleaching agents mentioned above, sodium hypochlorite and/or potassium hypochlorite may be most advantageously used, and the amount of sodium hypochlorite and/or potassium hypochlorite is preferably adjusted so that the amount of available chlorine in the fungicide is at least 0.3%, and preferably so that the amount of available chlorine is at least 0.5% and less than 4.5%. Actually, if the amount of available chlorine from the hypochlorous acid salt is under 0.3% the fungus bleaching effect will be inadequate; however, if the amount of the available chlorine is 0.5% or greater, killing and bleaching of the fungi can be expected within a waiting time of about 5 minutes. Conversely, if the amount of available chlorine increases to 4.5% or greater, it will be impossible to achieve gelatin and thus solidification of the resulting fungicide, despite the use of the gelling agent.

The use of a gelling agent in combination with the bleaching agent is essential for the fungicide of the invention. Suitable gelling agents include aliphatic carboxylic acids, and preferably alkali metal salts or ammonium salts of aliphatic carboxylic acids of 8-16 carbon atoms, and 1,2-hydroxystearic acid; these compounds may be used alone or in combinations of 2 or more.

Of the gelling agents mentioned above, particularly alkali metal salts of aliphatic carboxylic acids such as sodium stearate and sodium myristate may be most advantageously used, and the amount of the gelling agent in the fungicide is preferably adjusted so that the amount is 0.3-20%, and more preferably 0.5-10%. Actually, if the amount of the gelling agent is under 0.3% it will be impossible to adequately maintain the solid state of the fungicide, thus hampering its feeding out from the container during use. Conversely, if the amount of the gelling agent increases to 20% or greater, the fungicide will become too hard, preventing application of an adequate amount of the fungicide to the desired areas when used, and requiring repeated applications in order to apply the desired amount of the effective component.

The fungicide of the invention may have a variety of compositions which include the above-mentioned bleaching agent and gelling agent, but preferably comprises a base, an oxidation-type bleaching agent, a gelling agent, a surfactant, a humectant, a thickener and water.

The base is used in the fungicide of the invention for a two-fold function, i.e., for achieving the purposes of inhibiting growth of fungi and preventing decomposition of the oxidation-type bleaching agent, specifically of hypochlorous acid metal salts. Consequently, according to the invention, when the base is added to the fungicide its amount is preferably adjusted so that he final pH value of the fungicide is higher than 11, and more preferably in the range of 12-13.

Incidentally, from the viewpoint of inhibiting growth of fungi, it is desirable for the final pH of the fungicide to be higher than 11, or else lower than 2. This is because while fungi generally exhibit optimum cell activity at near pH =5-6, they can survive in most sections of substrates in the natural world with a wide pH range of 3-10, and especially in environments of high temperature (30°C or higher) and high humidity (80% RH or higher), fungi can easily survive in an even wider pH range of 2-11. Also, from the viewpoint of decomposition of the hypochlorous acid metal salt used as the bleaching agent, since these compounds undergo decomposition reaction more actively at near neutral, it is generally preferred for the amount of base added to be adjusted so as to produce a pH value at least higher than 11, and more preferably a pH value in the range of 12-13.

The surfactant used as necessary in the fungicide of the invention serves the purpose of improving the cleaning property, and any desired non-ionic, anionic, cationic or amphoteric surfactant may be used. Suitable surfactants which may be mentioned include, but are not limited to, the following examples: non-ionic surfactants such as alkyl phenols and ethylene oxide addition products; anionic surfactants such as alkylbenzene sulfonate, cationic surfactants such as alkyltrimethylammonium, and amphoteric surfactants such as amino acid types. The amount of surfactant to be added to the fungicide may be selected as desired.

The humectant which may also be used if necessary serves the purpose of preventing drying out of moisture during storage, and any common humectant may be used, including glycerine and polyethylene glycol. The amount of the humectant to be added may also be selected as desired depending on the need.

Also, the thickener is added for the purpose of complementing the gelling property to provide spreadability which an ensured a smooth, uniform distribution. Examples of thickeners which may be advantageously used in the fungicide of the

invention include, but are not limited to, the following: organic thickeners such as polyacrylic acid and polysaccharide compounds, and inorganic thickeners such as synthetic mica and synthetic smectite. In order to avoid generation of gas and a reduced fungicidal effect, it is necessary to select the thickener with attention not to cause an oxidation-reduction reaction with oxidation-type bleaching agent. The amount of thickener to be added may be selected as desired depending on the need.

Water is also essential in the fungicide of the invention for the purpose of permeation of the agents, for example, and the amount of water added is normally a balancing amount.

The fungicide of the invention may be prepared by combining the above-mentioned components in the desired manner. Preferably, a fungicide precursor is prepared by combining all of the components except the gelling agent in the desired order. Next, after adding the prescribed amount of the gelling agent to the precursor and heating to dissolution, it may be placed in a suitable frame for its preparation. Thus, a solid fungicide with the desired shape may be obtained.

The fungicide of the invention is preferably provided in solid form, and more preferably in stick form. The stick-shaped fungicide is preferably housed in a container in a manner which allows its gradual feeding out during use. The stick may have the shape of a smaller cylinder or small prism, but is preferably a small cylinder to allow easier feeding out from the container. If the stick is a small cylinder, its dimensions are preferably a 10-30 mm diameter and a 50-150 mm length for better handleability, but diameters of smaller than 10 mm may also be employed if necessary for use in narrow areas from which fungi are to be eliminated.

The fungicide of the invention may be applied for elimination of fungi in the same manner as, but more easily then, common fungicides. For example, for removal of fungi developing on bathroom walls, a prescribed amount of the fungicide is fed out from the stick container and applied so that the fungicide is rubbed onto the joint sections between wall tiles. A few applications of the fungicide, such as once or twice, will normally be sufficient, but repeated application is also possible if necessary. The fungicide may be adequately applied at a low thickness so long as the fungicide contacts the fungi. After the fungicide

has been applied, it is left to stand to allow sufficient action on the fungi. The standing time need only be a short time, usually about 5-6 minutes. Progress of the fungicidal effect may be easily confirmed in a visual manner based on fading of color of the fungi, i.e. depigmentation of the fungi. After the color of the fungi has faded, the fungicide adhering to the wall is removed by washing. An advantage of the fungicide of the invention is that it can be easily removed by water washing alone, and particularly, water washing may be advantageously accomplished by spraying lukewarm water onto the applied sections with a shower or the like. Subsequent drying may be achieved by allowing the sections to stand.

When carrying out the present invention, it is recommended to pre-apply running water or lukewarm water to wet the sites where fungi have developed, thus allowing the fungicide to permeate to the narrower sites where fungi have developed, for more effective removal of the fungi. Also, after the fungi have disappeared the series of fungicidal operations is completed by water washing, but in order to ensure no residual fungicide and to hasten completion of the washing, it is recommended to give consideration to the amount of gelling agent and thickener added, and in some cases to additionally use a water-soluble polymer which can provide an effect of complementing dissolution in water.

Examples

The present invention will now be further explained by way of examples. Note, in the fungicide samples produced in the examples, that the samples 2-1, 2-5, 2-6, 2-7, 3-1, 4-10 and 4-11 each represents a comparative example.

Example 1

The following reagent grade compounds were combined in the amounts indicated.

Sodium hypochlorite (available chlorine = 5%)	41.0 wt%
Sodium hydroxide	0.9 wt%
Sodium stearate	4.7 wt%
Sodium myristate	4.7 wt%
Water	48.7 wt%

The resulting mixture was placed in a glass container (washed commercially available mayonnaise bottle) and heated to 80-90°C. After completely dissolving the total amounts of the sodium stearate and sodium myristate, the resulting viscous liquid was packed into an oven-preheated plastic container for stick glue having an inner diameter of 21 mm and a depth of 50 mm, and allowed to cool to room temperature. A stick-shaped solid fungicide (available chlorine = 2.05%) was thus obtained.

The resulting fungicide was thinly applied to the fungi-rich joints of tiles in a bathroom and allowed to stand for 5 minutes. After application of the fungicide, the fungi color gradually faded, becoming virtually colorless after 5 minutes. Upon then spraying warm water from a shower onto the sites where the fungicide had been applied, complete washing and removal was possible without residue of the fungicide.

Example 2

Seven stick-shaped solid fungicides were prepared by mixing reagent grade sodium hypochlorite (available chlorine = 5%), reagent grade sodium hydroxide, reagent grade sodium myristate, synthetic smectite (trade name: SWN, product of Cope Chemical Co.), reagent grade polyethylene glycol (average molecular weight: 1000) and water in the (gram) amounts listed in Table 1 below, according to the procedure described in detail below. As shown in Table 1 below, the resulting fungicide samples 2-1 to 2-7 differed in their available chlorine contents (%).

Table 1

Sample No.	2-1*	2-2	2-3	2-4	2-5*	2-6*	2-7*
Available chlorine (%)	4.5	1	0.5	0.3	0.2	0.1	0.05
Water	0.5	35.5	40.5	42.5	43.5	44.5	45
Sodium hypochlorite	45	10	5	3	2	1	0.5
Sodium myristate	--	2.5	2.5	2.5	2.5	2.5	2.5
Smectite	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sodium hydroxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polyethylene glycol	1	1	1	1	1	1	1

* comparative example

First, the sodium hypochlorite aqueous solution, sodium hydroxide and synthetic smectite were added in their prescribed amounts to the prescribed amount of water, and mixed after placement in a glass container (washed commercially available mayonnaise bottle). Solutions with each of the components dissolved therein were obtained. For preparation of fungicide sample 2-1, the subsequent preparation steps were omitted since completely uniform dissolution of the components could not be achieved at this stage. For fungicide samples 2-2 to 2-7, sodium myristate was then added to the solution in the prescribed amounts, and the mixture was heated to 85-90°C. This gave viscous, milky white solutions. The resulting viscous solutions were each packed into an oven-preheated plastic container for stick glue having an inner diameter of 21 mm and a depth of 50 mm, and allowed to cool at room temperature. Stick-shaped solid fungicides (available chlorine contents listed in Table 1) were thus obtained.

Simulation fungicide test

The fungicidal action of each of the obtained fungicides (fungicide samples 2-2 to 2-7) were evaluated based on the degree of color fading.

After coloring a veneer panel violet by immersion in an aqueous pigment solution (violet #401, product of Daiwa Chemicals), each of the fungicides was thinly applied thereon as a stripe and allowed to stand for 5 minutes. The violet color of the veneer panel slowly faded after application of the fungicides. Visual

examination of the color fading from the veneer panel gave the results listed in Table 2 below.

Bathroom fungicide test

Fungicides (fungicide samples 2-2 to 2-4) whose effectiveness (satisfactory color fading) had been evaluated in the simulation fungicide test described above were thinly applied to the fungi-rich joints of tiles in a bathroom and allowed to stand for 5 minutes. After application of the fungicide, the fungi color gradually faded, becoming virtually colorless after 5 minutes. Upon then spraying warm water from a shower onto the sites where the fungicide had been applied, complete washing and removal was possible without residue of the fungicide. The results obtained are listed in Table 2.

Table 2

Sample No.	2-2	2-3	2-4	2-5*	2-6*	2-7*
Available chlorine (%)	1	0.5	0.3	0.2	0.1	0.05
Color fading	About 2 minutes	2-4 minutes	Almost totally faded	No color fading	No color fading	No color fading
Bathroom fungi	Disappeared	Disappeared	Almost totally disappeared	--	----	

*comparative example

As the above results clearly show, it is preferred for fungicides to have their compositions adjusted so that the available chlorine contents are within the ranges of the fungicides of the invention, i.e. it is preferred for sodium hypochlorite and (or) potassium hypochlorite to be added so that the available chlorine content is at least 0.3%, and even more preferred for sodium hypochlorite and (or) potassium hypochlorite to be added so that the available chlorine content is at least 0.5%. With an available chlorine content of under 0.3% the bleaching of the fungi will be

insufficient, while fungicides with available chlorine contents of at least 0.5% can offer bleaching and elimination of fungi within a waiting time of about 5 minutes.

Example 3

The procedure described in Example 2 was repeated. However, for this example 3 stick-shaped solid fungicides were prepared by combining reagent grade sodium hypochlorite (available chlorine = 5%), reagent grade sodium hydroxide, reagent grade sodium myristate, reagent grade polyethylene glycol (average molecular weight: 1000) and water in the (gram) amounts listed in Table 3 below, according to the procedure described in detail below. As shown in Table 3 below, the resulting fungicide samples 3-1 to 3-3 differed in their available chlorine contents (%)

Table 3

Sample No.	3-1*	3-2	3-3
Available chlorine (%)	4.5	3	2
Water	2	17	27
Sodium hypochlorite	45	30	20
Sodium myristate	2.5	2.5	2.5
Sodium hydroxide	0.5	0.5	0.5
Polyethylene glycol	1	1	

*comparative example

First, the sodium hydroxide was added in its prescribed amounts to the prescribed amount of water, and each mixture was placed in a glass container. Next, the prescribed amount of sodium myristate was added to the mixture which was then heated to 85-90°C. After then adding the prescribed amount of sodium hypochlorite the solution was heated to 85-90°C. All of the components dissolved, giving a viscous, milky white solution. For preparation of fungicide sample 3-1, the subsequent preparation steps were omitted since completely uniform dissolution of the components could not be achieved at this stage.

The resulting viscous solutions were each packed into an oven-preheated plastic container for stick glue having an inner diameter of21 mm and a depth of 560 mm, and allowed to cool to room temperature. Stick-shaped solid fungicides (available chlorine contents listed in Table 3) were thus obtained.

Simulation fungicide test

The fungicidal action of each of the obtained fungicides (fungicide samples 3-2 to 3-3) were evaluated by the procedure described in Example 2. The results obtained are shown in Table 4 below.

Bathroom fungicide test

The fungicidal action of the fungicide samples 3-2 to 3-3 were evaluated by the procedure described in Example 2. The results obtained are listed in Table 4.

Table 4

Sample No.	3-1*	3-2	3-3
Available chlorine (%)	4.5	3	2
Color fading	--	About 30 seconds	About 1 minute
Bathroom fungi	--	Disappeared	disappeared

*comparative example

As the above results clearly show, it is preferred for the fungicides to be prepared by adding sodium hypochlorite and (or) potassium hypochlorite so that the available chlorine content is less than 4.5%.

Example 4

The procedure described in Example 2 was repeated. For this example, however, eleven stick-shaped solid fungicides were prepared by mixing reagent grade sodium hypochlorite (available chlorine = 5%), reagent grade sodium hydroxide, reagent grade sodium myristate, synthetic smectite (tradename: SWN, product of Cope Chemical Co.), reagent grade and water in the (gram) amounts listed in Table 5 below, according to the procedure described in detail below. As

shown in Table 5 below, the resulting fungicide samples 4-1, to 4-11 differed in their sodium myristate contents (%).

Table 5

Sample No.	4-1	4-2	4-3	4-4	4-5	4-6	4-7	4-8	4-9	4-10*	4-11*
Sodium myristate (%)	20	15	10	7.5	5	2	1	0.5	0.3	0.2	0.1
Water	25.5	28	30.5	31.75	33	34.5	35	35.25	35.35	35.4	35.45
Sodium hypochlorite	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
Sodium myristate	10	7.5	5	3.75	2.5	1	0.5	0.25	0.15	0.1	0.05
Smectite	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sodium hydroxide	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

*comparative example

First, the sodium hypochlorite aqueous solution, synthetic smectite and sodium hydroxide were added in their prescribed amounts to the prescribed amount of water, and mixed after placement in a glass container. Next, the prescribed amount of sodium myristate was added to each solution which was then heated to 85-90°C. All of the components dissolved, giving a viscous, milky white solution.

Each of the resulting viscous solutions was packed into an oven-preheated plastic container for stick glue having an inner diameter of 21 mm and a depth of 50 mm, and allowed to cool to room temperature. As shown in Table 6, stick-shaped solid fungicides (sodium myristate contents listed in Table 5) were obtained with fungicide samples 4-1 to 4-8, and an approximately solid fungicide was obtained with fungicide sample 4-9. Fungicide samples 4-10 and 4-11 underwent considerable softening, so that the solid state of the fungicides could not be maintained.

Simulation fungicide test

The fungicidal action of the obtained fungicides (fungicide samples 4-1 to 4-9) was evaluated according to the procedure of Example 2. In this example, instead of the degree of color fading, the time (minutes) required for complete fading was measured. The results obtained are shown in Table 6.

Table 6

Sample No.	4-1	4-2	4-3	4-4	4-5	4-6	4-7	4-8	4-9	4-10*	4-11*
Sodium myristate (%)	20	15	10	7.5	5	2	1	0.5	0.3	0.2	0.1
Solid state	0	0	0	0	0	0	0	0	Approx-imately 0	X	X
Time to pigment fading	Ca.2 min.	Ca.2 min.	Ca.2 min.	Ca.2 min.	Ca.2 min.	Ca.2 min.	Ca.2 min	Ca.2 min.	Ca.2 min.	---	

*comparative example

As the above results clearly show, it is preferred for the fungicides to be prepared by adding the fatty acid alkali metal salts sodium stearate and sodium myristate so that the alkali metal salt content is in the range of 0.3-20%, and more preferably so that the fatty acid alkali metal salt content is in the range of 0.5-10%. When the fungicides contained these gelling agents at less than 0.3%, the solid state could not be adequately maintained, and it was difficult to feed out the container-housed fungicide during use.

Effect of the Invention

As explained above, by using a fungicide according to the invention, its effective component acts directly on fungi and kills them while also providing a newly cleaned surface by bleaching the action surface, to allow reliable fungicidal and cleaning operations through safe and easy use without waste.

What Is Claimed Is:

1. A solid fungicide characterized by containing an oxidation-type bleaching agent as an effective component and comprising a gelling agent for solidification of said bleaching agent.

2. A solid fungicide according to claim 1, characterized by being composed of a base, an oxidation-type bleaching agent, a gelling agent, a surfactant, a humectant, a thickener and water.

3. A solid fungicide according to claim 1 or claim 2, characterized in that said bleaching agent is at least one compound selected from the group consisting of alkali metal salts and alkali earth metal salts of hypohalogenous acids, halogenous acids and halogenic acids.

4. A solid fungicide according to any of claims 1 to 3, characterized in that said gelling agent is at least one compound selected from the group consisting of alkali metal salts or ammonium salts of aliphatic carboxylic acids of 8-16 carbon atoms, and 1,2-hydroxystearic acid.

5. A solid fungicide according to any of claims 1 to 4, characterized by being in the form of a stick and being housed in a container in a manner which allows its gradual feeding out during use.